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Raman and infrared spectra of 2,5-difluoro-and 2,4-difluoro nitrobenzene

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The infrared spectra of 2,4- and 2,5-difluoronitrobenzene in the liquid phase have been recorded for the first time in the region 250–4000 cm^{-1}. These studies have been supplemented by their Raman spectra excited by the 6328 Å Ne radiation from a He-Ne Laser. Measurement of the state of polarization of the Raman lines have been made and the observed vibrational frequencies have been assigned to different modes.

1. Introduction

In comparison to the vast amount of experimental work on the vibrational spectra of disubstituted benzenes containing the NO_2 group (vide all the references), the work on trisubstituted benzenes is rather scanty. It is also apparent from a survey of the literature that multi-homosubstituted benzenes are more thoroughly studied than the heterosubstituted ones. As a part of our program of studying a survey of the literature that multi-homosubstituted benzenes are more thoroughly studied than the heterosubstituted ones. As a part of our programme of studying the vibrational spectra of substituted nitrobenzenes (Shukla *et al* 1968, Shukla & Upadhya 1969) we have reported here the results of our studies on 2,4- and 2,5-difluoronitrobenzenes. The available spectroscopic study of these molecules is concerned with the electronic absorption spectrum in hexane solution.

2. Experimental Method

The samples of pure grade used in these experiments were obtained from E. Merck (Germany) and were used without further purification. These are liquids at room temperature and the infrared spectra were recorded using a film of the liquid between two CsBr windoks, with a Perkin-Elmer 521 Grating infrared spectrophotometer in the range 250–4000 cm^{-1}. The Raman spectra were obtained by the courtesy of Dr. N. Yellin, and were excited by the 6328 Å radiation of Ne from a He-Ne Laser source. Spectra have been taken of the scattered radiation polarized in the direction parallel and perpendicular to the incident

exciting beam, by using a polarizer. The polarization measurements were made from the two spectra from the same molecules.

3. Results and Discussions

The infrared and Raman frequencies of the two difluoronitrobenzenes are shown in figures 1 and 2*. Table 1 lists the absorption bands and the assignments

Table 1. Fundamental vibrational frequencies of 2,4- and 2,5-difluoronitrobenzene (cm^{-1})

2,4-difluoronitrobenzene			2,5-difluoronitrobenzene			Assignments	
Raman	Infrared	Int.+	Raman	Infrared	Int.+		
			146 d			$C-NO_2$ twisting	a''
293 d	293	2.5		274	2.5	C–C–C o.p. bending	a''
			370 d			C–F o.p. bending	a''
430 d			407 d	407	4.5	C–F o.p. bending	a''
454 d	454	1.1	454 d	456	1	$C-NO_2$ o.p. bending	a''
				480	1	C–C–C o.p. bending	a''
513 d	513	3	535 p	535	5	C–C–C i.p. bending	a'
618 d	618	8	643 p	642	2	C–C–C i.p. bending	a'
	676	2.5	671 d	672	4.5	C–C–C o.p. bending	a''
737 d	735	5	717 d			C–H o.p. bending	a''
748 d	750	7	754 p	754	7	C–F i.p. bending	a'
			780 p	775	9	C–F i.p. bending	a'
843 p	843	6.9	820 p	819	9	Ring breathing	a'
	861	8	830 p	834	9	$C-NO_2$ i.p. bending	a'
	827	5.5		872	7	C–H o.p. bending	a''
976 p	976	9	943 p	942	5.5	C–C–C trigonal bending	a'
1091 p	1090	8	1071 p	1070	3	C–H i.p. bending	a'
1141 p	1139	4	1137 p	1137	7	C–H i.p. bending	a'
1155 p	1155	8		1162	2.5	C–H i.p. bending	a'
	1194	2.5	1192 p	1192	9	C–F stretching	a'
1237 p	1237	4	1265 p	1264	9.5	C–F stretching	a'
1280 p	1283	10		1284	8	$C-NO_2$ stretching	a'
	1319	4	1300 p	1300	6	C = C stretching	a'
1350 p	1350	10	1349 p	1347	10	N = O stretching	a'
	1455	5		1436	7	C = C stretching	a'
1494 p	1493	5	1497 p	1496	10	C = C stretching	a'
1536 p	1536	9.6	1441 p	1440	10	N = O asymmetric stretching	a'
						C = C stretching	
1680 p	1610	10	1603 p	1603	6.5	C = C stretching	a'
	3081	6		3075	7	C = C stretching	a'
				3114	6	C = C stretching	a'

Abbreviations : o.p. = out-of-plane; i.p. = -in-plane; d = depolarized line; p = polarized line; int. = intensity.

+ Maximum intensity is 10.

* The Raman spectra in these figures are labeled as perpendicular to the incident radiation and parallel to the incident radiations, which imply perpendicular to the electric vector in the incident radiation and parallel to the electric vector in the incident radiation respectively.

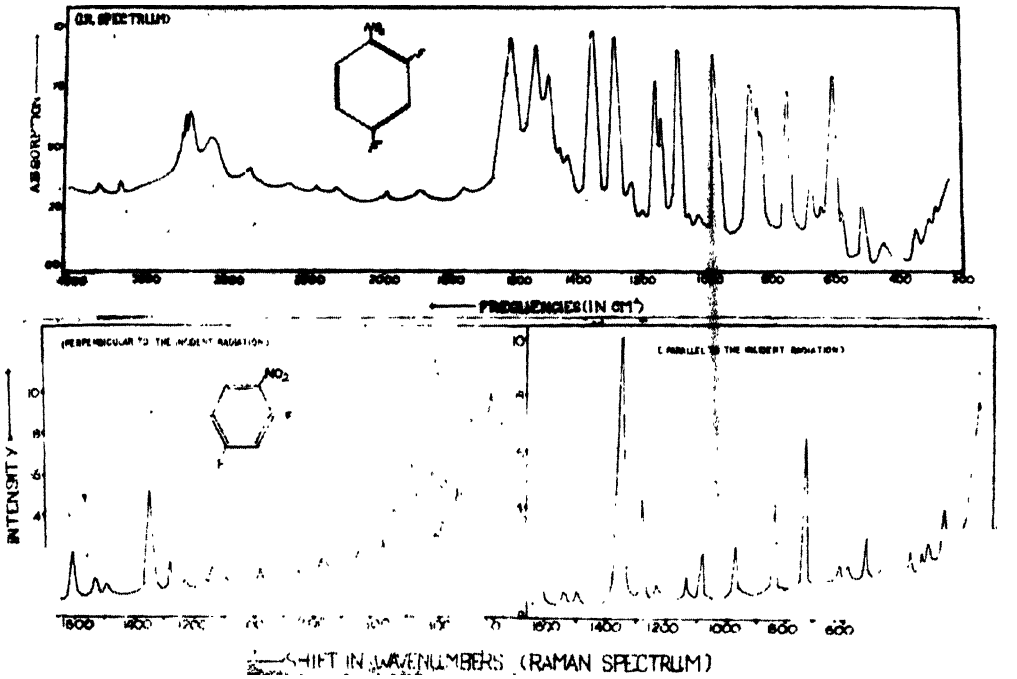

Fig. 1 The Infrared and Raman Spectra of 2,4-difluoronitrobenzne.

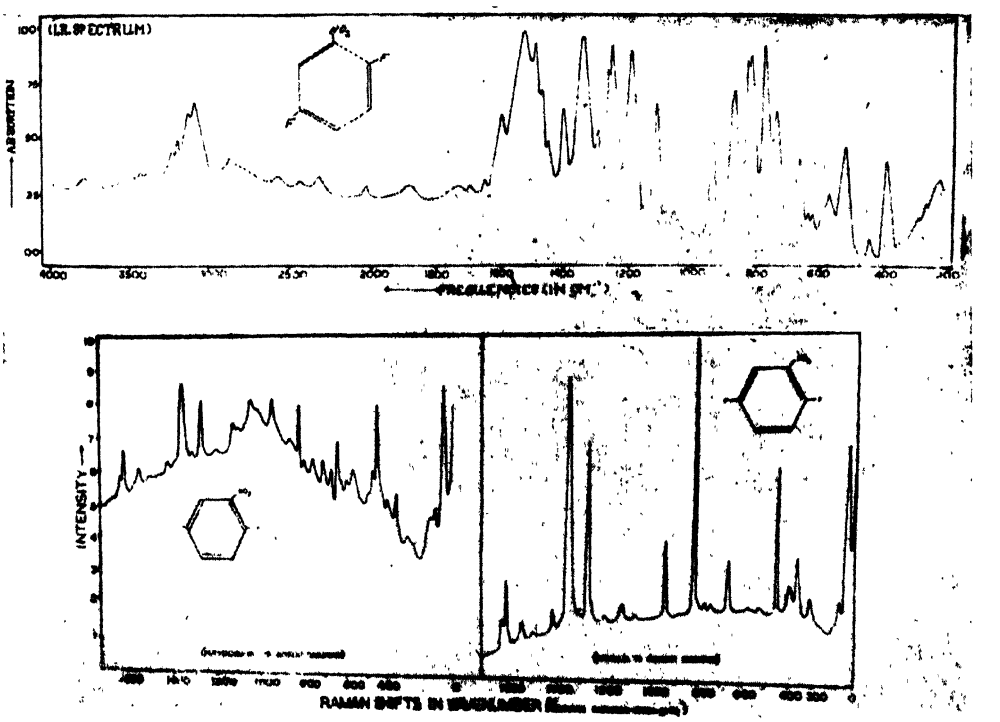

Fig. 2. The Infrared and Raman Spectra of 2,5-difluoronitrobenzene.

made. The NO_2 groups are assumed to lie in the plane of the ring, both these molecules would belong to the C_s point group. The thirty benzene—like fundamental vibrational modes would then be divided into 21 planar (a') and 9 non-planar (a'') vibrations. In addition there would be six fundamentals due to the internal vibrations of the NO_2 group ($4a'+2a''$) making a total of thirty six vibrations in all. All vibrations are active in infrared and Raman. The a'' vibrations would give rise to depolarized Raman lines. These two types of vibrations are discussed below under separate headings.

(A) *Benzene Type Vibrations*

(1) *C–H Vibrations* : Three C–H stretchings, three C–H in -plane bendings and three C–H out-of-plane bending modes are expected to appear in the spectra of these two molecules. The stretching vibrations are expected in the infrared region of 3000–3100 cm^{-1} and for 2,4-difluoronitrobenzene are assigned at 3075 and 3114 cm^{-1}. Only one peak is observed in the region at 3081 cm^{-1} for the other compound. The in-plane bending vibrations are expected to have magnitudes lying in the range 1050 to 1150 cm^{-1}, and are expected to be polarized in the Raman spectrum. On this basis the frequencies at 1091, 1140 and 1155 cm^{-1} for 2,4-isomer, and 1071 and 1162 cm^{-1} for the 2,5-isomer, respectively, have been assigned to these modes. Only two out-of-plane bending vibrations could be located, at 737 and 827 cm^{-1} for the 2,4-isomer and at 717 and 782 cm^{-1} for 2,5-isomer.

(2) *Skeletal Vibrations* : The various carbon vibrations in multisubstituted benzenes are characterized by different amounts of substitution effects, and hence the assignments are quite complicated. The doubly degenerate vibrations all split into two components and for C_s symmetry give rise to six polarized and two non-polarized Raman lines. The former arise from the vibrations at frequencies 1485, 1585 and 606 cm^{-1}, whereas, the latter arise from the 404 cm^{-1} vibration. In all cases one component lies at a lower frequency. From analogy with assignments for similar molecules from the group of vibrations at 513, 618, 1494, 1536, 1609 cm^{-1}, for 2,4-difluoronitrobenzene, the first two are assigned to the (C–C–C) vibration and the last three to the (C = C) mode. One component of the 1485 cm^{-1} (e_{1u}) vibration of benzene is observed at 1455 cm^{-1} in the infrared spectrum, but not observed in Raman spectrum. The corresponding frequencies in 2,5-difluoronitrobenzene at 535, 643, 1497, 1541 and 1603 cm^{-1} appeared in both the Raman and infrared spectra, while the band at 1436 appears only in the infrared spectrum. The assignment of the higher component of 404 cm^{-1} (e_{1u}) vibration is not clear as the (C–NO_2) rocking and (C–F) bending also appear in this region. The lower component is observed at 293 and 276 cm^{-1}, respectively, in the 2,4- and 2,5-compounds. Four non-degenerate vibrations give rise to three polarized and one unpolarized Raman lines. In the Raman

spectrum of 2,5-difluoronitrobenzene we have polarized lines at 820, 943, 1300 cm^{-1} and a non-polarized line at 671 cm^{-1}, and we have assigned them to the ring breathing, C–C–C in-plane bending, C–C stretching and C–C–C out-of-plane bending, respectively, corresponding to the frequencies 992, 1010, 1310 and 703 cm^{-1} of benzene. The similar lines for 2,4-difluoronitrobenzene are 843, 976, 1319 and 676 cm^{-1} respectively. Of these the last two are observed only in the infrared spectrum.

(3) *Vibrations of the Substituted Nitro Group* : Excluding the vibrations of the NO_2 group we expect six polarized and three depolarized Raman lines, corresponding respectively to the C–F and C–NO_2 stretching and planar bending modes and the C–F and C–NO_2 out-of-plane bending modes.

Both C–F and C–NO_2 stretching vibrations are found in the neighbourhood of 1250 cm^{-1} and unique assignments of the observed frequencies in this region are not possible. We have assigned the C–NO_2 stretching vibration at 1282 and 1264 cm^{-1} and the two C–F stretching at 1197, 1237 and 1192, 1265 cm^{-1} in 2,4- and 2,5-difluoronitrobenzene molecules. The 2,5-isomer frequencies observed at 830, 780 and 754 cm^{-1} are assigned to the one C–NO_2 and the two C–F in-plane bending modes. The C–NO_2 planar bending mode is assigned at 861 cm^{-1} in 2,4-isomer but only one C–F in-plane mode could be assigned at 748 cm^{-1}. A depolarized line is observed at 454 cm^{-1} in both the molecules and is assigned to the C–NO_2 out-of-plane rocking vibration. Only one C–F non-planar bending could be located at 430 cm^{-1} for the 2,4-isomer, whereas bands observed at 370, 407 cm^{-1} have been assigned to the same mode in the other molecule.

The six internal vibrations of the NO_2 group give rise to four polarized and two depolarized Raman lines. Polarized lines observed at 1350 and 1536 cm^{-1} for the 2,4- and at 1349 and 1541 cm^{-1} for the other isomer have been assigned to the N = O symmetric and asymmetric stretching modes respectively. The higher frequencies appear as broad peaks in the spectra due to superposition of a C = C stretching vibration arising as the second component of the 1585 cm^{-1} vibration of benzene. A highly depolarized Raman line at 146 cm^{-1} in 2,5-difluoronitrobenzene has been assigned to the C–NO_2 twisting vibration. The other internal vibrations could not be assigned due to overlapping in the region of their expected appearance.

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